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The dissociation energy of CN and C₂

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The dissociation energies of CN and C₂ are determined with multireference configuration-interaction calculations utilizing very large Gaussian basis sets. Valence level one-particle errors, such as basis set incompleteness and basis set superposition error, are essentially eliminated by extrapolation. The errors in the correlation, or *n* particle, treatment are considered in detail. The effect of 1*s* correlation is computed using the averaged coupled-pair functional approach. Our best estimate for C₂ is in very good agreement with the recent experimental result by Urdahl *et al.* Our best *D*₀ value for CN is 7.72±0.04 eV. This is larger than previous theoretical values and in good agreement with the recent experimental result (7.738±0.02 eV) of Huang *et al.* The origin of the differences between the current *D*₀ and our previous theoretical value is discussed.

I. INTRODUCTION

The CN radical is important in studies of stellar atmospheres, molecular cloud chemistry, comets, and flame chemistry. Observations of CN have been through either the red ($A^2\Pi-X^2\Sigma^+$) or violet ($B^2\Sigma^+-X^2\Sigma^+$) emission systems. In many stars, the nitrogen abundance is deduced from the CN abundance and is therefore extremely sensitive to the CN dissociation energy and its oscillator strength (*f*₀₀). Using such a model, Sinha and Tripathi¹ suggested that a range of values between 7.66 to 7.76 eV is consistent with the solar CN→C+N equilibrium abundances. Lambert *et al.*² originally adopted a *D*₀ of 7.60 eV, but revised³ the value to 7.69±0.05 eV using the theoretical value of Bauschlicher, Langhoff, and Taylor⁴ for the oscillator strength (*f*₀₀=2.36×10⁻³) of the red system. In 1992, using the same oscillator strength, but newer values for the C and N abundances, Grevesse and Sauval⁵ concluded that a *D*₀ value of 7.77 eV was most consistent with the solar data. Very recently Sauval, Blomme, and Grevesse⁶ concluded that this oscillator strength was consistent with a *D*₀ value of 7.90–8.00 eV, which is clearly too large. They therefore used a larger oscillator strength (3.25×10⁻³), which implies a *D*₀ of 7.85 eV. These *D*₀ values⁶ deduced from the solar data are inconsistent with the most recent experimental determinations.^{7,8} Costes *et al.*⁷ obtained a value of 7.77±0.05 eV by studying the C(³P)+NO(²Π)→CN(²Σ⁺)+O(³P) reaction via crossed molecular beams and by probing the CN(²Σ⁺) product by laser-induced fluorescence (LIF). Huang *et al.*⁸ determined the heat of formation of CN from the spectroscopic threshold for C₂N₂+*hν*→2CN. Using this CN heat of formation and the C and N heats of formation from Wagman *et al.*⁹ yields a CN *D*₀ value of 7.738±0.02 eV.

The *D*₀ value for CN was determined to be 7.65±0.06 eV using *ab initio* calculations⁴ corrected using analogous calculations on N₂ and the well known experimental¹⁰ dissociation energy of N₂. The error bars represented an 80% confidence limit. This value for the CN dissociation energy is smaller than those deduced from the solar models or from the most recent experiments.

The accuracy of *ab initio* calculations has been con-

stantly improving over the past few years. One area of improvement has been in estimating the one-particle limit. Using the correlation consistent basis sets developed by Dunning and co-workers,¹¹ supplemented with diffuse functions to describe the induced moments, Woon¹² observed that the dissociation energies of the weakly bound rare gas dimers converged logarithmically with improvement in the basis set. This observation allowed him to extrapolate his computed results to the basis set limit. Independently, Bauschlicher and Partridge¹³ and Peterson *et al.*¹⁴ applied this approach to the calculation of the dissociation energy of N₂. While the two groups used different series of correlation consistent basis sets, the extrapolated values agreed to within 0.1 kcal/mol. These results clearly support the use of this extrapolation procedure for strongly bound molecules.

Bauschlicher and Partridge¹³ also showed that the effect of 1*s* correlation could be computed using a size-extensive approach. With the ability to reach the basis set limit and to account for inner-shell correlation, the largest error in modern calculations is in the correlation treatment. However, full configuration interaction (FCI) calculation have given some insight into this problem.¹⁵

Because of the improvements in accuracy and the importance of the CN dissociation energy in stellar modeling, we have reinvestigated its dissociation energy. While our previous calculations on N₂ give some insight into the accuracy of the present calculations for CN, the fact that carbon *sp* hybridizes while nitrogen does not results in some concerns as to the applicability of the N₂ results to CN. However, the recent LIF study of rotational levels by Urdahl *et al.*¹⁶ yields an accurate C₂ *D*₀ value of 6.297±0.02 eV. Thus it is now possible to use both C₂ and N₂ to calibrate our CN calculations, which should allow us to determine if carbon *sp* hybridization introduces any additional complications in accurately treating CN.

II. METHODS

We use the (augmented) correlation-consistent polarized-valence [(aug)cc-pV] basis sets of Dunning and co-workers.¹¹ The triple-zeta (TZ), quadruple zeta (QZ), and quintuple zeta (5Z) basis sets are utilized. A cc-pV6Z basis

TABLE I. The carbon cc-pV6Z basis set. For the *s* and *p* spaces, the exponents and contraction coefficients for the 1*s*, 2*s*, and 2*p* orbitals are given. When no contraction coefficients are given, the functions are uncontracted.

<i>s</i> ^a			<i>p</i> ^a	
Exp	Coeff(1 <i>s</i>)	Coeff(2 <i>s</i>)	Exp	Coeff(2 <i>p</i>)
312 229.0	0.000 006	0.000 001	478.641 5	0.000 062
46 749.69	0.000 044	0.000 009	113.418 4	0.000 537
10 638.55	0.000 232	0.000 049	36.816 23	0.002 926
3 013.287	0.000 979	0.000 209	13.964 92	0.011 503
983.046 4	0.003 550	0.007 600	5.807 870	0.035 721
354.887 7	0.011 439	0.002 454	2.435 940	0.093 120
138.403 4	0.033 002	0.007 202	1.173 779	
57.361 84	0.083 996	0.018 795	0.553 675	
24.928 38	0.180 684	0.043 249	0.262 173	
11.229 64	0.304 989	0.082 621	0.123 617	
5.201 549	0.341 288	0.128 518	0.056 671	
2.426 564				
0.967 344				
0.445 599				
0.197 122				
0.086 347				
Exponents for polarization functions ^b				
<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	<i>i</i>
5.558 400	2.862 909	3.126 000	1.905 510	1.509
2.316 000	1.192 879	1.340 000	0.793 962	
0.965 000	0.497 033	0.558 333		
0.402 083	0.207 097			
0.167 535				

^aThe (16*s*11*p*) primitive set [H. Partridge, J. Chem. Phys. **90**, 1043 (1989)] is used with the contraction coefficients taken from the C ³P SCF orbitals.

^bOptimized even-tempered polarization sets with β fixed at 2.4.

set is developed for carbon in an analogous manner to the cc-pV6Z set developed for nitrogen in Ref. 13. The contracted [7*s*6*p*5*d*4*f*3*g*2*h*1*i*] basis set is tabulated in Table I. As shown below, the cc-pVQZ basis set yields a good description of CN, and is the starting point for the study of 1*s* correlation. The seven inner 1*s* functions are contracted to two functions using the coefficients given by Dunning.¹¹ The outer five *s*-type functions are left uncontracted as are the six *p*-type functions. Two tight *d* functions with exponents 5.262 and 14.984 and two *f* functions with exponents 4.152 and 12.147 are added to carbon. The nitrogen core basis set is developed in an analogous manner and is described in detail in our recent study¹³ of N₂. Only the pure spherical harmonic components of the basis functions are used.

The orbitals are optimized using the complete active space self-consistent-field (CASSCF) approach. The 2*s* and 2*p* orbitals are included in the CASSCF active space, except in the calibration calculations where the active space is expanded—these calculations are described in detail below. When the red system is studied, a state-averaged (SA) CASSCF procedure is used to optimize the orbitals for the *A* and *X* states. More extensive correlation is included using the multireference configuration-interaction (MRCI) approach. All configurations in the CASSCF wave function are used as references in the MRCI calculations. The same reference space is used when 1*s* correlation is treated. The MRCI reference space is different in some of the calibration calculations and this is discussed below. The effect of higher exci-

TABLE II. Summary of spectroscopic constants of CN as a function of basis set.

Basis	<i>r_e</i> (<i>a</i> ₀)	<i>D_e</i> (eV)	<i>D₀</i> (eV)	<i>ω_e</i> (cm ⁻¹)
	ICMRCI			
cc-pVTZ	2.231	7.471	7.344	2044
cc-pVQZ	2.222	7.686	7.558	2054
cc-pV5Z	2.220	7.752	7.625	2058
cc-pV6Z	2.219	7.779	7.651	2064
aug-cc-pVTZ	2.230	7.524	7.398	2037
aug-cc-pVQZ	2.222	7.710	7.582	2056
aug-cc-pV5Z	2.220	7.763	7.636	2061
Basis	ICMRCI+ <i>Q</i>			
	<i>r_e</i> (<i>a</i> ₀)	<i>D_e</i> (eV)	<i>D₀</i> (eV)	<i>ω_e</i> (cm ⁻¹)
cc-pVTZ	2.232	7.426	7.299	2040
cc-pVQZ	2.224	7.649	7.521	2048
cc-pV5Z	2.222	7.718	7.591	2054
cc-pV6Z	2.221	7.746	7.618	2059
aug-cc-pVTZ	2.232	7.479	7.353	2035
aug-cc-pVQZ	2.224	7.674	7.546	2052
aug-cc-pV5Z	2.222	7.730	7.602	2057
Expt.				
	2.214 ^a		7.738±0.02 ^b	2068.6 ^a
			7.77 ±0.05 ^c	

^aReference 10.

^bReference 8.

^cReference 7.

tations is accounted for using either the multireference analog of the Davidson corrections (denoted +*Q*) or using averaged coupled-pair function (ACPF)¹⁷ approach. In most calculations internal contraction¹⁸ (IC) is utilized to keep the calculations manageable.

The *r_e* and *ω_e* values are computed using a parabolic fit in 1/*r* using a very tight grid to minimize the uncertainty in the reported values. The basis set superposition error (BSSE) is computed using the counterpoise technique¹⁹ including the full ghost basis set. The internally contracted calculations are performed using the MOLPRO set of programs^{18,20} while the unconstrained MRCI calculations are performed using the SEWARD/SWEDEN set of programs.^{21,22}

III. RESULTS AND DISCUSSION

We report the results of our calculations as a function of basis set expansion in Tables II and III for CN and C₂, respectively. The convergence of *r_e* and *ω_e* with basis set improvement is very good and the results in the largest basis set are in good agreement with experiment. We note that the convergence of the *ω_e* value is not as smooth as the other properties; we suspect that this arises from using only a parabolic fit of three points to compute the spectroscopic constants. The small differences between the computed results and experiment are consistent with the expected effect of 1*s* correlation, and we do not consider these results further.

Unlike the *r_e* and *ω_e* values, the *D₀* values are clearly not converged with respect to expansion of the one-particle basis set. The basis set limit is estimated by fitting the logarithm of the incremental energy improvements vs basis set size—see Fig. 1. This approach leads to the conclusion that

TABLE III. Summary of spectroscopic constants of C₂ as a function of basis set.

Basis	$r_e(a_0)$	$D_e(\text{eV})$	$D_0(\text{eV})$	$\omega_e(\text{cm}^{-1})$
ICMRCI				
cc-pVTZ	2.366	6.087	5.972	1841
cc-pVQZ	2.357	6.244	6.130	1851
cc-pV5Z	2.354	6.291	6.177	1853
cc-pV6Z	2.354	6.310	6.195	1854
aug-cc-pVTZ	2.366	6.117	6.003	1837
aug-cc-pVQZ	2.357	6.261	6.146	1850
aug-cc-pV5Z	2.355	6.306	6.191	1854
ICMRCI+Q				
cc-pVTZ	2.367	6.014	5.899	1840
cc-pVQZ	2.358	6.175	6.061	1846
cc-pV5Z	2.356	6.224	6.110	1848
cc-pV6Z	2.355	6.244	6.129	1849
aug-cc-pVTZ	2.367	6.042	5.928	1832
aug-cc-pVQZ	2.358	6.192	6.077	1845
aug-cc-pV5Z	2.356	6.232	6.118	1849
Expt.				
Expt. ^a	2.348		6.216±0.13	1854.7
Expt. ^b			6.297±0.02	

^aReference 10.^bReference 16.

the CN ICMRCI valence one-particle limit is 0.015 ± 0.003 eV larger than that computed using the cc-pV6Z basis set. For C₂ the basis set limit is 0.008 ± 0.002 eV larger than that obtained with the cc-pV6Z basis set. The BSSE error must go to zero as the basis set becomes complete and the computed results are consistent with this expectation; the computed CN BSSE is 0.033, 0.022, 0.011, and 0.006 eV for the

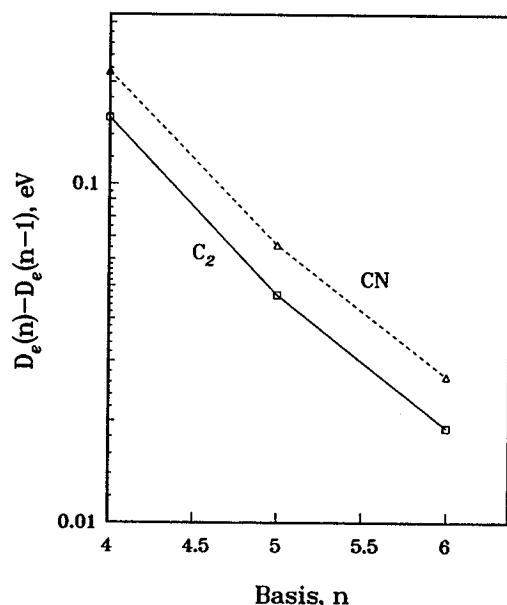


FIG. 1. A semi-log plot of the improvement in D_e with basis set improvement. The n describes the basis set size: 3 through 6 represent the cc-pVTZ, cc-pVQZ, cc-pV5Z, and cc-pV6Z basis sets, respectively.

TABLE IV. Summary of results for study of 1s correlation. The quantities are in eV. The basis set developed for core correlation is used (see the text).

	D_e		
	ICMRCI	ICMRCI+Q	ICACPF
CN			
9-e ^a	7.570	7.534	7.538
13-e	7.641	7.593	7.589
ΔE	0.071	0.059	0.051
C ₂			
8-e	6.258	6.189	6.201
12-e	6.348	6.270	6.268
ΔE	0.090	0.081	0.067
Basis set superposition error			
CN			
9-e	0.022	0.024	0.023
13-e	0.023	0.025	0.024
C ₂			
8-e	0.021	0.022	0.022
12-e	0.022	0.023	0.023

^aIndicates the number of electrons correlated, e.g., 9-e indicates that only the nine valence electrons are correlated.

cc-pVTZ, cc-pVQZ, cc-pV5Z, and cc-pV6Z basis sets, respectively.

The results of the calculations including 1s correlation are summarized in Table IV. The change in the basis set superposition with the inclusion of inner-shell correlation is very small. As for N₂, we find that the 1s effect decreases when the size-extensive ICACPF method is used. Because calculations with different number of electrons are being compared, we feel that the ICACPF is our most accurate value for the 1s effect on the dissociation energy. The computed 1s effect for CN (0.051 eV) falls between that for C₂ (0.067 eV) and that for N₂ (0.037 eV¹³). This trend is consistent with the contraction of the 1s orbital with increasing Z. We estimate the uncertainty in the 1s effect as the difference between the ICACPF and ICMRCI+Q values; this leads to 0.051 ± 0.008 eV for CN and 0.067 ± 0.014 eV for C₂.

We next consider the errors in the n -particle treatment. A calibration calculation for N₂ showed that the FCI value²³ fell between the ICMRCI and ICMRCI+Q results. Consistent with this calibration, the final ICMRCI and ICMRCI+Q values¹³ bracketed the experimental value. For C₂, FCI calculations²⁴ show that the true value will be between the MRCI and MRCI+Q, but very close to the MRCI value. Thus our best value for the D_0 of C₂ is obtained by adding the 1s effect (0.067 ± 0.014 eV) and the residual one-particle error (0.008 ± 0.002 eV) to the cc-pV6Z ICMRCI value; this yields 6.270 ± 0.016 eV. (Where the error bars do not account for any uncertainty associated with the n -particle treatment.) This is in very good agreement with the recent experimental value of 6.297 ± 0.02 eV. The ICMRCI+Q value of 6.204 eV, is clearly too small, as expected based on the FCI calibration. The difference between our best estimate and experiment suggests that our uncertainty in the ICMRCI n -particle treatment is 0.03 eV or less.

There have been no FCI calibration calculations for CN, but on the basis of our C₂ and N₂ results alone, we suspect that the true value will fall between the ICMRCI and ICMRCI+*Q*, and be closer to the ICMRCI value. We test this hypothesis by performing some *n*-particle calibration calculations using the cc-pVTZ basis. First we note that internal contraction introduces only a very small (0.004 eV) error in the computed *D_e*. This is very similar to the 0.003 eV contraction error found for C₂.

Expansion of the active space is tested as follows. Only the nine valence electrons are correlated. The natural orbitals are determined using an SCF based singles and doubles CI calculation. On the basis of the natural orbital occupation numbers at *r_e* and infinite separation, the active space was expanded, relative to the 2*s* and 2*p* active space, to include two additional *σ* orbitals, one additional *π* orbital, and a *δ* orbital. The MRCI reference list included all occupations where any of the component configurations had an absolute value greater than 0.01 in the CASSCF wave function. The MRCI calculations identified an additional configuration with a coefficient greater than 0.02 in the MRCI wave function, which was also added to the reference space. The final MRCI calculations were performed with 121 reference occupations yielding 3 699 784 configuration state functions. This treatment yields a *D_e* value of 7.480 and 7.483 eV at the MRCI and MRCI+*Q* levels, respectively. The small difference between the MRCI and MRCI+*Q* levels for the large active space suggests that we have a very balanced treatment of *r_e* and infinite separation and hence should have a result that is close to the *n*-particle limit for the *D_e* value. The ICMRCI value obtained with the smaller active space is 7.471 eV, which is in good agreement with the larger active space results. The ICMRCI+*Q* result (7.426 eV) is significantly smaller. Thus the calibration calculations demonstrate that the true value is expected to be quite close to the ICMRCI result. As in the case of C₂, the correct value might even be slightly larger than the ICMRCI result. On the basis of the CN *n*-particle calibration and our results for N₂ and C₂, we assign an uncertainty of ±0.03 eV to the ICMRCI value as arising from limitations in the *n*-particle treatment.

Our final CN *D₀* value is determined as the cc-pV6Z ICMRCI value, plus the estimate of one-particle incompleteness, the computed 1*s* effect, and the uncertainty in the *n*-particle treatment. This approach yields 7.72±0.04 eV. This value is in good agreement with the value of 7.738 ±0.02 eV obtained by Huang *et al.*⁸ It suggests that the true *D₀* value must lie in the lower half of the experimental range (7.77±0.05 eV) obtained by Costes *et al.*⁷ It also suggests that the value (7.85 eV) deduced by Sauval, Blomme, and Grevesse⁶ is too large.

In light of the good agreement of our computed *D₀* value with the recent experimental values^{7,8} and the poor agreement with the most recent value deduced from solar data.⁶ We have recomputed the radiative lifetime of the red system using the SA-CASSCF/ICMRCI approach in conjunction with the aug-cc-pVQZ basis set. The *ΔG_{1/2}* values are about 10 cm⁻¹ smaller than experiment,¹⁰ which is consistent with the neglect 1*s* correlation¹³ and with the limitations in the

valence basis set (see Table II). The *T₀* value is only in error by 66 cm⁻¹. Using the theoretical potentials, shifted to bring the *T₀* value into agreement with experiment, and the ICMRCI transition moment yields a lifetime of 11.3 μs. This is only about 1% longer than our previous value.⁴ Using the aug-cc-pVTZ basis set instead of the aug-cc-pVQZ basis set results in essentially no change in the transition moment at 2.2 *a₀*; that is, the one-particle basis set is essentially converged for the calculation of the transition moment. If the SA-CASSCF transition moment is used, the lifetime is 9.5 μs; it is therefore clear that more extensive correlation increases the lifetime and thus our ICMRCI value should be a lower bound to the radiative lifetime. We conclude that an *f₀₀* of 2.33×10⁻³ is the best value for the red system. It is clear that additional work on the solar models for CN is required.

We should note that the results of this work were communicated to Grevesse and Sauval. Using our present *D₀* and *f₀₀* values, they varied the C and N abundances and the temperature within their estimated uncertainties and found²⁵ that it was possible to reproduce the solar data. This supports our conclusion that our results form a consistent and accurate set of data and that more work on the solar models is required.

While the current value overlaps with our previous theoretical value⁴ (7.65±0.06 eV), it is clear that the older value was too small. Part of this arises because the errors due to neglect of 1*s* correlation are not proportional to the *D₀* values; the *D₀* of N₂ is 1.26 times that of CN, while the effect of 1*s* correlation on the *D₀* of N₂ is only 0.73 times that in CN. In addition the calibration of the *n*-particle treatments shows that the ICMRCI is the best value for CN, while the best value is between the ICMRCI and ICMRCI+*Q* results for N₂. These small differences between CN and N₂ resulted in the underestimation of the CN dissociation energy in our previous work. These differences between CN and N₂ are now specifically accounted for in the present work, and therefore the biggest uncertainties in the previous work have been eliminated.

IV. CONCLUSIONS

We have studied CN and C₂ using high levels of theory. Our best dissociation energies are determined by extrapolating to the valence limit, accounting for 1*s* correlation effects, and accounting for the uncertainty in the correlation treatment. Our best *D₀* value for C₂ is 6.27 eV, which is in good agreement with the recent experiment of 6.297±0.02 eV. Our best value for CN is 7.72±0.04 eV. This is in good agreement with the experimental value (7.738±0.02 eV) from Huang *et al.*⁸ The calculations also suggest the true *D₀* must lie in the lower half of the experimental range (7.77 ±0.05 eV) obtained by Costes *et al.*⁷

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